

# **The evaluation of an analytical protocol for the determination of substances in waste for hazard classification**

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## **Summary**

The classification of waste as hazardous could soon be assessed in Europe using largely the hazard properties of its constituents, according to the the Classification, Labelling and Packaging (CLP) regulation. Comprehensive knowledge of the component constituents of a given waste will therefore be necessary. An analytical protocol for determining waste composition is proposed, which includes using inductively coupled plasma (ICP) screening methods to identify major elements and gas chromatography/mass spectrometry (GC MS) screening techniques to measure organic compounds. The method includes a gross or indicator measure of 'pools' of higher molecular weight organic substances that are taken to be less bioactive and less hazardous, and of unresolved 'mass' during the chromatography of volatile and semi-volatile compounds. The concentration of some elements and specific compounds that are linked to specific hazard properties and are subject to specific regulation (examples include: heavy metals, chromium(VI), cyanides, organo-halogens, and PCBs) are determined by classical quantitative analysis. To check the consistency of the analysis, the sum of the concentrations (including unresolved 'pools') should give a mass balance between 90 and 110 %. Thirty-two laboratory samples comprising different industrial wastes (liquids and solids) were tested by two routine service laboratories, to give circa 7 000 parameter results. Despite discrepancies in some parameters, a satisfactory sum of estimated or measured

concentrations (analytical balance) of 90 % was reached for 20 samples (63 % of the overall total) during this first test exercise, with identified reasons for most of the unsatisfactory results. Regular use of this protocol (which is now included in the French legislation) has enabled service laboratories to reach a 90 % mass balance for nearly all the solid samples tested, and most of liquid samples (difficulties were caused in some samples from polymers in solution and vegetable oil). The protocol is submitted to French and European normalisation bodies (AFNOR and CEN) and further improvements are awaited.

Keywords: Waste composition; analysis; substances; mass balance; hazard status

## 1. Introduction

The classification of waste as hazardous is required for regulatory compliance. The Seveso II Directive considers the toxicity and ecotoxicity of waste. The last Waste Directive (Directive 2008) defines 15 hazard properties, mainly based on the properties of substances and the Classification, Labeling and Packaging of substances and mixtures regulation (CLP 2008). Waste will be considered as a mixture of substances, and their properties assessed by calculation from the properties of their component substances (total content), or from specific tests. Since tests are not available for all criteria, the classification of waste as hazardous will commonly be based on computation from the concentration of substances identified in the waste. We have not found in the literature a method or a group of methods that provides a ‘total’ measure of the concentration of elements and substances in a waste and evidence that no important elements or substances have been left out.. We have not found analytical mass balances of waste. Authors use different methods for different classification. By example, for WEEE, the characterisation uses infrared spectroscopy for polymers identification, and ICP for metals (Stanval et al 2013). For household waste, the identification of remnants of objects is used (Dahlén and Lagerkvist 2008). Simplified waste index are then proposed as surrogate of full composition and classification (i.e. Gupta and Babu 1999). Another way is to derive mineralogical forms of the elements from leachate composition at different pH and geochemical modeling (Van der Sloot and Kosson 2012). Without that knowledge, the most sophisticated algorithm for hazard classifications relies up till now on hypothesis: “To demonstrate the feasibility of the proposed algorithm for waste classification, nine hypothetical composite wastes, each containing five chemicals

with known human toxicity, physicochemistry, ecotoxicity and exposure potential...” (Musee et al 2008).

Another approach is to develop specific human toxicity (biological) tests (Weltens et al 2012, Deprez et al 2012).

The authors mention that the chemical characterization is only useful if toxic content is known or suspected. For most of the waste arriving at the eco-industries facilities, there is not enough accompanying information to suspect with precision toxic substances that could then be looked for at the lab. An approach for Hazard Property 14 is to combine ecotoxicological battery of test and partial chemical analysis (Ribé 2012). Nevertheless, the observed toxic effect exerted by the assessed waters did not always correlate with measured levels of contaminants or the chemical measures of bioavailability, e.g. leached fraction. This question arises frequently, and it is only with a full knowledge and speciation of elements in water that correlation between concentration of compounds and ecotoxicity can be found (Postma et al 2009). That is why a general and exhaustive method for waste analysis, corresponding to the present proposal of DG Environment of the EU for waste classification, is proposed here.

In summary, many methods are devoted to the determination of the total content of one particular analyte or some parameters, which are important for the environment and subject to regulation. On the other hand, the determination of the leachable content is essential in risk assessment. Here, the complete composition of the waste is looked for, to assess the (intrinsic) hazard, with some insurance that some important part of the waste would not have been left over. This paper explores the use of an analytical protocol to determine the total composition of a waste by its component elements and substances. The approach has been applied to 15 solid and 17 liquid wastes by two test laboratories. The paper presents the analytical results obtained by using the protocol and discusses some limits and improvements of the proposed approach and summarizes the classification of the wastes tested according to Seveso II regulation. The protocol is embedded in the Seveso II French regulation for waste treatment facilities (MEDDTL 2011) and is currently being discussed at the French Standard Association (AFNOR 2012). The protocol is submitted to European normalisation bodies (CEN) and improvements are proposed, in particular the use of more standards (up to 86 in October 2012) to quantify more precisely the volatile and semi-volatile compounds. The protocol can be used for classification according to the update of the European Waste Directive and the European List of Waste. Up to summer 2012, more than 150 samples have been analysed according to this protocol, mainly by eco-industries. A second paper will detail the method for speciation of mineral elements in mineral substances, and the classification of those wastes for different hazardous properties (H 4, 5, 6, 7, 8, 10, 11, 13 and 14) of wastes.

## 2. Methods

### 2.1 OVERVIEW OF THE METHOD

An analytical protocol is proposed which allows the user to gain an appropriate knowledge of the organic and mineral substances in a waste and enable the determination of their properties for regulatory or recycling purposes. The protocol has been tested on a number of wastes using two test laboratories to ensure it is fit for purpose. A number of revisions were made to improve the approach which uses a combination of quantitative methods, screening methods and in the case of organics parameters gross measures of the ‘pools’ of unresolved composition. The mass balance achieved is at least 90 %. Using this methodology it is possible essentially quantify the composition of waste samples in terms of specific substances. The protocol is still in progress.

Hazard classification can then be performed, by transforming the stoichiometric total element content into appropriate mineral compounds or species and then applying the hazard properties for these compounds listed in the CLP regulations. This approach can be used to provide an assessment of waste hazard status.

Current practice for waste analysis is predominantly focused on the accurate identification of specific pollutants for compliance with specific regulations (for example, polychlorobiphenyls - PCB and total petroleum hydrocarbons - TPH). An alternative approach is to use indicator or gross measures to provide information on groups of substances (for example: total organic carbon, suspended solids, extractable substances, leachable substances and percolating substances). Where the pooled components constitute a considerable proportion of the total full (e.g percent levels) this could impact on the reliability of the resulting waste classification.

This paper presents a more global approach to waste classification which is outlined in Figure 1. The use of “screening” analytical techniques can be used to determine elemental and organic composition. The results are commonly presented as “semi-quantitative”, especially in waste extracts, because in practice it is not possible to calibrate the apparatus for all the analytes. These techniques will be applied here hence the concentration level

triggering classification as hazardous are frequently in the 0.1 – 10 % range, and that at such high concentrations the relative error of semi-quantification seems reduced (see Result section). New analytical parameters were defined. For solid waste, “non extractible organic compounds” is the mass lost by calcination of the dried solid residue that remains after the extraction of semi-volatile substances. The aim is to quantify the content of cellulose, lignin, polymers and organic compounds with high molecular weight, which are assumed to be non hazardous. For solid and liquid wastes, the parameters “unidentified volatile compounds” and “unidentified semi-volatile compounds” are calculated from the unresolved chromatographic areas of the chromatograms. The water content, the sum of total major elements and metals content, the ash content minus the sum of the metal concentrations, the sum of the volatile and semi-volatile compounds and the sum of unidentified organic compounds could represent a large fraction of the mass of the sample. Carbonates are not taken into account (Figure 1). Anions (total halogens, free and bound cyanides, chromium(VI)) are measured separately (they may be present) to compute possible mineralogical phases of the elements. Elements of importance for hazard assessment (for example, heavy metals, chromium(VI), cyanides, organic substances with specific regulation like PCBs, PAHs) are measured quantitatively when they may be present. CEN standardized methods are preferred where available. The results allow classification according to different regulations (Waste Directive, Seveso II Directive etc.).

During the analytical campaign testing 32 wastes, some amendments were made to the protocol, although they were not always applied by the laboratories, in particular the quantitative methods for individual chlorinated compounds (necessary for accurate classification) and the use of 3 response factors for chromatographic calibration (necessary for better mass balance). One amendment was added after the testing campaign.

## **2.2 ANALYTICAL PROTOCOL**

### Quality / Accreditation

It is recommended that analyses should, as far as possible, be carried out under ISO 17025 accreditation. The analytical methods should also, where possible be characterized in terms of: range of validity and the limit of quantification, precision, accuracy, reproducibility, linearity and specificity. Characterized and accredited

methods should be indicated. For data from non-standard methods, the method of extraction (where applicable) and the method of concentration quantification should be summarized.

### Sampling

Appropriate standards for waste sampling must be followed to obtain a suitable laboratory sample. A Framework Standard and 5 associated technical reports which provide guidance on waste sampling are available from the work of TC 292- Waste Characterisation (EN 14899 and CEN/TR 15310-1 to -5). If a sampling plan is not developed in accordance with this standard and guidance the waste producer should follow commonly used procedures or industry standards for the waste being sampled. The sampling program should generate a suitable laboratory sample.

### Laboratory sample

The test sample should be prepared from the laboratory sample according to the requirements of standard EN 15002. In particular, when multiple immiscible phases or fractions are present, the analysis should be performed on each phase and the results may be recombined according to the proportions of each phase in the original sample to provide the final result.

A sample with a paste like consistency is considered to be a solid sample if after drying in air at or below 40 °C for 48 hrs maximum, pre-treatment (e.g. sieving and grinding) are possible. If the paste like state is maintained after 48 hrs it should be considered as a liquid and must be analyzed as such.

### Analysis of liquid waste

In case of presence of suspended solids or separated phases, and when it is suspected that the analytical methods applied to the liquid sample may not extract and quantify the compounds present in any solid phase particles or in dual phases, the sample must be separated into its component fractions by a suitable method (filtration, centrifugation, decantation), the mass of each fraction determined, and comprehensive analysis of the separated liquid fraction and solid fraction or each phase performed (EN 15002). The measurements required under the protocol are:

- Density

- Water content (EN 14346): heating at 105 °C or Karl-Fisher assay depending on the sample and the presence of volatile substances. The completion of the test by either method must be able to measure the water content up to 99.9% (to determine the levels of substances other than water from 0.1%, which is a classification limit value)
- Ash content by calcination at 550 °C (EN 15169)
- pH, redox potential (expressed as  $p_e = E_h \text{ (mV)}/59.16$ ) and electrical conductivity must be measured directly in the water for waste water and aqueous waste. For pastes and oil, the measurements are performed after a water extraction of the crude sample with a ratio of 10 l  $\text{kg}^{-1}$  dry matter in a closed container to limit exchange with the atmosphere. The measurement can then be performed after one hour of agitation in the liquid phase after simple decantation. The method (water extraction or direct measurement) should be clearly identified in the analytical report.
- If the waste is saline (conductivity  $> 0.15 \text{ S m}^{-1}$ ), it is preferable, to ensure a correct identification of the speciation of metals, to measure the chlorides and preferably all the halogens that are soluble in water. This can be done directly in the liquid waste (contaminated water and aqueous waste) or in the extract of 10 l  $\text{kg}^{-1}$  DM (pastes and oil). This assay does not interfere with the mass balance because the halogens are taken into account in the ash content.
- If the presence of cyanide is suspected, it is advised that free and complexed cyanide are determined separately following EN ISO 14403 or ISO 11262 or where this is not possible according to NF T 90-107, or an equivalent method.
- A total dissolution method must be used for the determination of major metals and elements (for example, silicon, sulphur and phosphorus). Partial dissolution methods like aqua regia EN 13657 are not appropriate. The measurement of major elements can be performed by AES-ICP (atomic emission spectrometry inductively coupled plasma) or other methods that provide a measure of total mineral elements or at the very least, a semi-quantitative measure (with the results expressed as a range of minimal and maximal concentration) (e.g.. EN 15309).
- The 12 heavy metals listed in the “European Landfill Directive” As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se and Zn) must be determined individually and quantitatively, with a total dissolution method.
- If the presence of chromium(VI) is suspected, it is recommended to measure it following NF T90-043, or an equivalent method.

- Determine the volatile substances and semi-volatile content by extraction and assay, if possible using a method characterized with the following characteristics:
  - calibration of volatiles: using at least one standard (e.g. toluene), 3 standards are preferred (e.g. toluene, trichlorethylene, hexane).
  - calibration of semi-volatiles: using at least one standard (e.g. fluoranthene) although three standards are preferred (e.g. C10, C25 and C40).
  - identification rate above 70%.
  - in the case of non-discrimination of isomeric substances, the result should be expressed as the sum of isomers and the CAS number of the most toxic isomer assigned.
  - if several substances have not been separated, the result should be expressed as the sum of the substances and the CAS number of the most toxic substance assigned.
  - the volatile organohalogenes should be determined individually and quantitatively.
  - the parameters "unidentified volatile compounds" and "unidentified semi-volatile compounds" should be calculated by integrating the unresolved chromatographic area 'the mass' of the chromatogram of volatile and semi-volatile compounds.
  - if one or more petroleum fractions are present, they should be quantified with the appropriate standards, excluding the unresolved chromatographic area. The mass of unidentified volatile and semi-volatile compounds without the petroleum fraction should then be calculated.
  - if the waste oil contains vegetable oils this should be esterified before injection so that the fatty acid products are detected in the semi-volatile determination. Otherwise, this oil will not be detected. Information on the potential presence of vegetable oil should be provided in advance by the holder of the waste.

Particular substances controlled by regulations with limit values  $< 1\%$  w/w should be determined if they are suspected to be present by classical quantitative analysis.

#### Expression of the results of liquid waste

All results should be expressed as the mass of substance per mass of raw sample. The results in mass per unit volume (e.g.  $\text{mg l}^{-1}$ ) should be converted to mass per unit mass ( $\text{mg kg}^{-1}$ ) using the density value. CAS numbers



should be reported where applicable. In case of analysis of separate fractions of a sample, the results should be issued for each fraction and mention the mass and the proportion of the fraction.

#### Mass balance of liquid waste

The sum of the water content, ash content (minus the metal contribution and other elements), metals and other elements, volatiles and semi-volatiles, "unidentified volatile compounds" and "unidentified semi-volatile compounds", and any oil fractions should reach 90 % of the gross weight of the test sample. If the water content exceeds 90% of the gross weight, then the sum of the aforementioned parameters should reach 50% of the mass of the sample which is not water. This last limit reflects the fact that the anions (halogens, oxides, carbonates etc.) which in some cases accompany the metal cations are not all measured in the protocol, to keep the protocol as simple and cost effective as possible. Laboratories may ideally continue to undertake additional investigations to improve the mass balance.

#### Analysis of solid waste

The test measurements are as follows:

- As an option, measure the bulk density of the laboratory sample without pretreatment (to give more insight about the nature of the waste).
- Water content (EN 14346): 105 °C drying or Karl Fisher depending on the waste and the rate of volatile substances.
- Pre-treatment (not for volatile compounds) by air drying at 40 °C, grinding, sieving, and measure of the content of residual water at 105 °C in the pretreated sample on a separate aliquot (EN 15002). If the size of the larger particle of the laboratory sample is greater than 5 cm, it is imperative to dry - grind - sieve – and mix at least 30 kg of the test sample followed by a second grinding – sieving – mixing operation to achieve a particle size of less than 250 µm for sub-samples of <1 g (see e.g. EN 13656 below).
- Content of the ash (calcinated residue) by calcination at 550 °C (EN 15169). For particularly heterogeneous waste and that cannot easily be ground to 200 µm, the measurement of the ash at 550 °C should be performed with a pretreated test sample of at least 10 g and ideally 30 g, using a gradual rise in temperature to avoid rapid burning, and with a cup with lid pierced with a hole for venting.

- pH, redox potential (expressed as  $p_e = E_h \text{ (mV)}/59.16$ ) and electrical conductivity should be measured in a water extract of crude sample with a ratio of  $10 \text{ l kg}^{-1}$  dry matter for solids, pastes and oil. The measurement can be performed after one hour of agitation in the liquid phase after simple decantation. The water extraction method must be clearly detailed in the report.
- If the waste is saline (conductivity of leachate  $> 0.15 \text{ S m}^{-1}$ ), it is desirable, to ensure correct speciation of metals, to measure the chlorides and preferably all the halogens in the water extract (see above). This assay does not interfere in the mass balance because the halogens are soluble in water and are taken into account through the ash content.
- If the presence of cyanide is suspected, it is advised that the free and complexed cyanide are determined separately according to ISO 11262 Soil quality - Determination of cyanide.
- Major Metal content and other elements (silicon, sulfur, phosphorus etc.) a total dissolution method must be used (for example CEN/TR 15018 or EN 13656). Using partial dissolution as aqua regia EN 13657 is excluded. The measure of major elements can be performed by AES-ICP (atomic emission spectrometry inductively coupled plasma) or other method providing total mineral elements in a manner at least semi-quantitative (eventually under the form of a range of minimal and maximal concentration).
- The 12 heavy metals (listed in the “European Landfill Directive” As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se and Zn) must be determined individually and quantitatively, with a total dissolution method.
- If the presence of chromium(VI) is suspected, it is recommended that this is measured by ionic chromatography after alkaline extraction (EN 15192).
- Determination of the volatile and semi-volatile content using an extraction and assay, if possible by a method characterized with the following attributes:
  - calibration of volatile: at least one standard (e.g. toluene), 3 standards are preferred (e.g. toluene, trichlorethylene, hexane);
  - calibration of semi-volatile: at least one standard (e.g. fluoranthene), 3 standards are preferred (e.g. C10, C25, C40);
  - identification rate above 70%;
  - in case of non-discrimination of isomeric substances, the result is expressed as the sum of isomers and the CAS number of the most toxic isomer should be assigned;

- if several substances are not separated, the result should be expressed as the sum of the substances and the CAS number of the most toxic substance assigned
- the volatile organohalogens should be determined individually and quantitatively;
- the parameter "non-extractable organic substances" is calculated as follows: the solid residue after extraction of semi-volatile substances is subject to evaporation of residual solvent and eventual remaining water, calcination (EN 15169) and weighed. The mass lost on ignition is considered as "non-extractable organic substance" and is related to the dry mass of the aliquot. The aliquot for the extraction of semi-volatile substances must not have been subject to water extraction.
- If one or more petroleum fractions are present, they should be quantified with the appropriate standards, apart from the unresolved chromatographic area. The mass of unidentified volatile and semi-volatile compounds without the petroleum fraction should then be calculated.
- Particular substances controlled by regulations with limit values < 1 % w/w should be determined if suspected by classical quantitative analysis.

#### Expression of results for solid waste

The water content is reported on the wet material ( $= (\text{water}) / (\text{water} + \text{solid})$ ). The concentrations of other substances are reported on dry matter basis (corresponding to the dry matter at 105 °C). The content of residual water at 105 °C of the pre-treated portion should be measured and taken into account to express the result on dry matter. CAS numbers are reported where applicable.

#### Mass balance of solid waste

The sum of the concentration of substances reported on a dry matter basis excluding the water content but including ash content less metals and other elements, metals and other elements, content of volatiles and semi-volatile substances and non-extractable organic substances, and any petroleum fractions) should reach 90% of the dry solids of the sample as determined by the dry matter test. Laboratories may ideally continue to undertake additional investigations to improve the mass balance.

## **2.3 ANALYTICAL METHODS USED BY THE SERVICE LABORATORIES**

As the protocol is intended for routine use, the analyses were intentionally performed by two commercial service laboratories. In the protocol the choice of some methods is left open to the user, and in the analysis campaign some methods that are specified in the protocol were not followed. Others were more precisely defined during the campaign. Some deviations from the protocol and some details for the analysis of total elements and heavy metals are presented at Table 1. Semi-quantitative ICP / MS or AES means that only a few elements are calibrated using standard solutions and then a simple response factor is applied to each element. This means that spectral interferences between elements are not (completely) eliminated in the calculation.

The pH and pe values were measured by INERIS (the author's Institute) for the solid samples on a leachate with a ratio of 10 l water/ kg DM, for oily/hydrophobic liquid samples on a water extraction at a ratio of 10 l water/ kg waste, and for "waste water" by direct measurement. Chloride was measured by INERIS by ion selective electrode in the same extracts. Chromium(VI) was analysed only for samples with high total chromium content, and by Lab2 only. The content of chromium(III) was calculated by difference between total chromium and chromium(VI). All the concentrations are expressed in % (weight/wet weight) for liquids and % (weight/dry weight) for solids.

For all parameters, results "lower than a limit of quantification" were attributed the arithmetic value of their limit of quantification.

## **2.4 SAMPLES AND PRETREATMENT**

The professional associations for hazardous waste handling (SYVED, SYPRED) proposed, in consultation with the French Ministry of Ecology (MEDDTL), a list of wastes to be studied. They sent laboratory samples to INERIS. The professional association of hydraulic binders (ATILH) added two samples of alternative fuels for cement kilns. These samples were intended to be representative of the 'pool' of wastes collected (constitution of primary samples, mixing - homogenization, quartering, and so on, to produce a laboratory sample of about 5 kg

or 5 litres). Among these samples, three shredded packaging and contaminated materials were received, in 200 liter drums. A large range of 15 solid and 17 liquid wastes covering most types of industrial wastes (listed in Table 2) have been studied.

The laboratory samples were pretreated according to EN 15002 by INERIS. When two phases (liquid and solid) were present, they were separated by settling or filtration. Each phase was analyzed separately. Fine grained samples (<1 mm) were put in 4-litre pots and mixed by rotation for at least an hour. Coarse-grained samples (with a particle size < 20 cm) were treated as follows:

- raw (as received) fraction without pre-treatment: a representative aliquot of fresh material was bottled in a 4 liters glass bottle, for analysis undertaken on the crude product (volatile compounds and water content).
- fraction pretreatment: a representative sub-sample is dried in an oven at 40 °C until it is dry enough to be ground in a jaw crusher or knife grinder to obtain a fine particle size (< 2 mm), is bottled, is mixed for one hour by rotation, and subsample is taken for the analysis (residue on ignition, metals, semi-volatile organic compounds).

Liquid samples were vigorously mixed by hand until no visual heterogeneity was seen, and sub-sampled.

The results of the "raw" and "pretreated" sub-samples are normally simply aggregated. The results of analysis of sub-samples from phase separation were recombined in the relative proportions of the phases in the original sample. In that way, a total of 37 samples and subsamples were produced per laboratory. For the sake of clarity, all results presented in this paper are for initial 32 samples and we have combined data where sub-samples were generated.

### **3. Results and discussion**

Full and detailed results are available (Hennebert, 2011).

### 3.1 PH, PE, WATER AND ASH CONTENT, ELEMENTS AND METALS

The results of pH and pe (redox potential) are presented in Table 3, ordered by decreasing pH. Results for chromium(VI) and (III) are reported for the 7 samples with the highest concentration of total chromium. The wastes cover a wide domain of acidity/alkalinity and redox status.

The water contents (by gravimetry or chemimetry) are presented at Figure 2, with values for Lab2 as a function of the values of Lab1 on a log/log scale. Results were consistent above 1% of water, but less so below. The ash content is the complement of the loss on ignition (LOI) measured according to standard NF EN 15169 . The results were shown at Figure 3. A good match of results was reached for this parameter between the two laboratories.

The determination of major and minor elements by ICP is semi-quantitative in the applied protocol with the exception of the 12 “heavy metals” and Si which have been quantified individually. The semi-quantitative analytical test data for each laboratory are expressed into concentration ranges (different for each laboratory). The center of the range was taken as the ‘result’ for that parameter. The concentrations were summed for each sample at Table 5 and 6 and used individually for each sample in Figure 4. Comparison of the two data sets showed a difference between laboratory for individual element data (bilateral Mann-Whitney tests, paired samples, 1088 pairs of data,  $p < 0.05$ ) but no difference for the sum of the elements (same test, 32 pairs,  $p < 0.05$ ). The correlation between the two laboratories was obvious but could be improved for some test samples and elements. The results of chromium(VI) are presented at Table 3.

Limits of quantification from 0.1 to 10 mg kg<sup>-1</sup> (depending on the waste matrix ) for mercury and 0.1 and 5 mg kg<sup>-1</sup> for cadmium have been reported, and have therefore been used . Given the potential impact of the concentration of cadmium and mercury on the classification of waste hazard status, it is recommended that a limit of quantification of 1 mg kg<sup>-1</sup> is achieved for these elements.

## **3.2 NON-EXTRACTIBLE ORGANIC COMPOUNDS (SOLID SAMPLES),**

### **VOLATILE AND SEMI-VOLATILE ORGANIC COMPOUNDS**

The “non extractible organic compounds” is the mass loss at 550 °C ( $\pm 25$  °C) of the dry mass of the sample after extraction of semi-volatile compounds. Lab1 performed a water extraction prior to semi-volatile extraction and conducted calcinations at 500 °C instead of 550 °C (Table 1). The results are presented in Figure 5 and Table 5. Some results of Lab1 appeared to be over-estimates (S1 to S5) or underestimates (S8-TRI).

The volatile and semi-volatile organic compounds were combined because the same compounds were sometimes assigned by laboratories in different analytical groups. Lab1 conducted further analysis "Total hydrocarbons C10-C40" on the liquid samples, but not the "unidentified semi-volatile organic compounds". Lab2 used the bottle "fresh" or "raw" for the analysis of semi-volatiles, instead of using the pretreated sample bottle and computed the "unidentified semi-volatile organic compounds" of liquid samples as "integration > C10". Therefore, direct comparison of "unidentified semi-volatile organic compounds" was not possible between laboratories.

The results for volatile organic compounds and semi-volatile compounds are presented individually in Figures 6 and 7, and as a sum in Tables 5 and 6. The list of detected compounds was not consistent between the two laboratories. Where there is agreement with compound identification the concentrations were not consistent between the two laboratories at concentrations below 0.1 %. It is considered that the data could be improved using a three standard calibration rather than a single standard. Comparison of the two data sets showed a difference between laboratory for individual compounds data (bilateral Mann-Whitney tests, paired samples, 424 pairs of data,  $p < 0.05$ ) but no difference for the individual compounds  $> 0.1$  % (same test, 62 pairs,  $p < 0.05$ ) and for the sum of the compounds (same test, 32 pairs,  $p < 0.05$ ).

The comparability in the test data between the two laboratories should be improved. The combination of two detectors (MS and FID) in parallel could assist in better matching. It should be noted that a therapeutic substance was detected by the two laboratories at low concentrations in a solvent from a pharmaceutical industry, showing that a fine detection of specific compounds is still possible. If a petroleum mixture is identified, it could be

quantified with a corresponding standard, and the corresponding surface subtracted from the response for unidentified compounds.

It should be noted that, for liquid samples, the result of the “unidentified semi-volatile compounds” can be easily controlled by a simple test. For each sample, an aliquot of weighed crude product was heated to 200 °C in an oven for 4 hours and weighed. The temperature of 200 °C was selected because it corresponds to the boiling point of n-undecane (n-C11). The computed difference [residue at 200 °C - sum of measured semi-volatile organic substances - ash content at 550 °C] provided a good match with the “unidentified semi-volatile compounds” (results not shown).

Further analyses of substances important in relevant regulation were performed for some samples, by routine quantitative methods at the laboratories. The sample of non-halogenated solvent was rich in methanol (S15, 4.3 %, mean of the two laboratories), followed by the sample of waste hydrocarbon mixture (S13-SCO, 0.27 %) and the sample of halogenated solvent (S14-SAN, 0.15%). The results were consistent between the two laboratories. Dioxins and furans concentrations between 100 and 500 ng TEQ/kg were observed for ash, bottom ash and APC residue of incineration of industrial and municipal waste, except for an APC bicarbonate residue (S1), showing a concentration of 20 000 ng TEQ/kg in the two laboratories. The following analyses were performed only by Lab2. Isocyanates were investigated for samples S14-PCX, S14-SAN, S14-SAR and S15 but not detected ( $< 1 \text{ mg kg}^{-1}$ ). Organic lead derivatives (tetramethyl and tetraethyl) were investigated in samples S9-SAR, S10, S11, S12-SON, S13-SCO, S13-SON and S18 and similarly not detected ( $< 25 \text{ mg kg}^{-1}$ ). Total PCBs (sum of 7 congeners) were found in the alternative fuel solid (S18,  $8 \text{ mg kg}^{-1}$ ), in a packaging and contaminated materials (S8-SAR,  $1.3 \text{ mg kg}^{-1}$ ) and a waste of hydrocarbon mixture (S13-SCO,  $1.05 \text{ mg kg}^{-1}$ ). The limits of quantification were relatively high for S9-SAR, S10, S11, S12-SON, S13-SON ( $< 35 \text{ mg kg}^{-1}$ ) and S14-PCX ( $< 46 \text{ mg kg}^{-1}$ ) and should be lowered since they were too close from the classification limit ( $50 \text{ mg kg}^{-1}$ ).



### 3.3 ORGANIC COMPOUNDS WITH CAS NUMBER AND ANALYTICAL MASS BALANCE

The number of organic compounds with CAS numbers and the associated cumulated concentrations are summarized in Table 4.

For some samples, a significant number of organic compounds were detected (up to 117) with a cumulated concentration from 0 to 82 %. This result is important to expand the basis for subsequent waste classification.

The analytical mass balances for the solid samples are presented in Table 5. Values between 90% and 110% are highlighted in yellow. The calculated parameter "ash content - sum of metals" is highlighted in orange when it is negative.

For Lab1, in three out of four cases where the mass balance is less than 90%, the "ash content minus the sum of metal" was negative. This was related to samples of shredded packaging containing contaminated materials and indicated insufficient homogeneity of the laboratory sub-sample as seen by the visual high heterogeneity of the samples. This also suggested that the sub-sample was not crushed and sieved finely enough and shows the importance of following standard pre-processing techniques and preparation of large test samples i.e. at least 30 kg of a material. To measure the calcinated residue, a test portion of about 30 g of ground material is recommended for shredded packaging and contaminated materials. For the measurement of metals, a test of not less than 1 g of secondary crushed sample should be used. It is imperative that laboratories control the value of "ash content minus the sum of metal" to detect and correct analytical errors.

The mass balance lay between 90% and 110% in 10 cases out of 15 samples for Lab1 and Lab2 (67%). This seemed satisfactory for a first trial of the protocol by a routine service laboratory which included deviations from the recommended methods. For comparison, a program of analysis of solid and liquid recovered fuels led by ATILH in 2009/2010 (Report INERIS DRC-109 459-14290A), showed that the median of the sum of known substances (the analytical mass balance) for 64 samples was 46% by weight.

The analytical mass balances of the liquid samples are presented in Table 6. Values between 90% and 110% are highlighted in yellow. The calculated parameter "ash content - sum of metals" is highlighted in orange when it is negative.

Lab1 reported the volatile hydrocarbons as C5-C10 (volatile Total Petroleum Hydrocarbons) and the sum of C10-C40 compounds (i.e. TPH) as the results for "unidentified volatile compounds" and "unidentified semi-volatile compounds" respectively. The mass balances are therefore not strictly comparable. On the side of mineral analysis, some results of "ash content minus the sum of metal" are negative. It is imperative that laboratories ensure strict compliance with the standard method of calcination, and improve the measurement of major elements.

The mass balance relied between 90% and 110 % in 10 cases of 17 for Lab1 and 9 cases of 17 for Lab2 (respectively 59 % and 53 % of the samples). Although encouraging the comparability of these results could be improved. When the water content is > 90%, the sum of known compounds exceeded half of the dry matter in 3 out of five samples for Lab1 and 1 case out of 6 for Lab2.

For hydrocarbons containing vegetable oil (sample S17 as informed by ATILH after the campaign), the method needs further development. Oily waste likely to contain vegetable oil should be saponified before injection so that the fatty acid products are detected in the group of semi-volatile. Otherwise, this oil will not be detected. Information on the potential presence of vegetable oil should be provided in advance by the holder of the waste. On the other hand, polar compounds are not measured in routine in the protocol. If they are suspected of being present, they should be measured by a specific method.

In conclusion it was possible to complete the mass balance using the new pooled parameter approach. Despite discrepancies for some parameters, a satisfactory analytical balance of 90 % was reached for 20 samples of 32 (63 %) during this first trial. Technical improvements to improve the majority of unsatisfying results have been identified.

### **3.4 CLASSIFICATION OF WASTE AS HAZARDOUS ACCORDING TO THE SEVESO II DIRECTIVE**

For hazard assessment according to the Seveso II Directive (using concentration limits of the Dangerous Preparation Directive – DPD 1999), the total metal content must first be converted into relevant mineral species, since the hazard properties are defined for mineral compounds rather than on an elemental basis. A first conservative estimation was performed by arithmetically by converting the total content of each element into the most hazardous form, taking into account the stoichiometry of the elements in the waste sample (Rebischung, 2011). To do that the hazard properties of the each of the potential for each element in terms of human or environmental toxicity were used as listed in the CLP regulation (CLP, 2011). For this process a number of minerals can be excluded on the basis of pH, pe and knowledge of inputs into the waste stream and the conditions of its generation.

The content of organic and mineral compounds were then summed according to their intrinsic hazard properties, and the total concentrations in each risk group were compared with the limit values (taking into account the additivity of some hazard properties) in the CLP regulation. This exercise was done with generic limit values given by the CLP and also, in a second assessment, with additional minimal aquatic ecotoxicity values  $EC_{50}$  from the literature (no evaluation of those  $EC_{50}$  was performed). The resulting classification of the waste (hazardous for human toxicity – class T+ and T and hazardous for aquatic environment – class N R50 and N R51) was as follows:

Using the CLP data without  $EC_{50}$  data and M factors of the CLP (M is a multiplier that lowers the limit of concentration triggering the classification as hazardous), 23 out of 32 samples were not classified as hazardous using the two sets of data (one set per laboratory), 4 were classified as hazardous by both sets of data (although this is largely due to different substances), 1 was classified as hazardous by both sets of data (but for a different hazard), and 4 were classified as hazardous by only one set of data;

Using additional  $EC_{50}$  data and the M factors recommended in the CLP, 13 out of 32 samples were not classified as hazardous for the two sets of data, 14 were classified as hazardous by both datasets, and the remaining 5 were classified as hazardous by only one set of data (largely because different substances were identified by the two

test laboratories, and secondly because of the differing concentrations reported). It is interesting to note that the studied samples are all classified as hazardous (when the information is available) with an absolute entry code by the European List of Waste (see Table 2, samples with an asterisk) and that they are not all classified as hazardous by calculations from the elements and substances composition from the protocol. In conclusion using the full CLP data and method, 27 samples out of 32 (84 %) of the samples were classified identically by the two laboratory data sets, despite differences in detected substances and concentration.

## **4. Conclusion**

A set of 32 samples were analyzed by two test laboratories, giving a total of 7 000 data points, from which chemical mass balances were calculated. Despite some deviations to the prescribed analytical protocol, the mass balance lied between 90 and 110% for 20 samples out of the 32 (63%) of the samples. As a result of this testing exercise the protocol has been amended during the testing program to improve on this encouraging initial result. A first exploratory classification of 32 wastes was performed with the protocol data. Twenty-seven samples out of 32 (84%) of the samples would have been identically classified using the two sets of laboratory data.

A first version of the protocol is included in a French application guideline of the Seveso II Directive (MEDDTL 2011). The eco-industries started in autumn 2011 on a wider analysis campaign ( $\pm 100$  samples), which may give rise to additional improvements that can be made to the protocol to ensure its effective application for a wider variety of wastes (i.e. waste from electric and electronic equipment - WEEE).

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**Table 1: Some analytical methods used by the laboratories**

| Item                                 | Lab1   | Lab2   |
|--------------------------------------|--|--|
| Calcination                          | Temperature of 500 °C  |  |
| Total elements and heavy metals      | <p>Solid samples: bomb combustion digestion or hydrochloric and nitric acid (aqua regia) digestion in an open tube, and semi-quantitative assay by ICP / MS for 33 elements and Hg. Si was determined after alkali-fusion.</p> <p>Liquid samples: bomb combustion digestion and screening (full-scan semi-quantitative assay) by ICP / MS for 33 elements and Hg was used.</p> <p>For the 12 heavy metals, an aqua regia digestion was performed and ICP/AES assay used.</p> | <p>Solid samples: (i) for major elements, mineralization of 0.5 g subsample by hydrochloric and nitric acids (aqua regia) for 2 h at 99 °C and semi-quantitative assay ICP / AES for 40 elements, or mineralization of 0.1 to 0.2 g subsample by alkali-fusion with lithium metaborate and tetraborate, dissolution in dilute nitric acid and semi-quantitative ICP / AES assay for 40 elements; (ii) for Si, analysis by volatilization with hydrofluoric acid gravimetry; (iii) for Hg, aqua regia digestion, cold vapor atomic fluorescence; (iv) for As, Se, aqua regia digestion, graphite furnace atomic adsorption; (v) for other heavy metals, aqua regia digestion, ICP /AES assay.</p> <p>Liquid samples: (i) for major elements, mineralization by hydrochloric and nitric acids (aqua regia) for 2 h at 99 °C and screening ICP / AES for 40 elements, (ii) for Si, analysis by volatilization with hydrofluoric acid gravimetry; (iii) for S, mineralization in the oxygen bomb and ion chromatography assay; (iv) for Hg, aqua regia digestion, cold vapor atomic fluorescence; (v) for As, Se, aqua regia digestion, graphite furnace atomic adsorption; (vi) for other heavy metals, aqua regia digestion, ICP /AES assay.</p> |
| Chromium(VI)                         |  | Solid samples: colorimetry   |
| Calibration of volatile compounds    | Use of one standard (toluene)  |  |
| Unidentified volatile compounds      | Replaced by volatile total petroleum hydrocarbon C5-C9   |  |
| Unidentified semi-volatile compounds | Replaced by total petroleum hydrocarbon C10-C40  |  |
| Non-extractable organic substances   | The aliquot has been subject to water extraction resulting in an over-estimation of the “non extractable organic substances”.  |  |

**Table 2 : Waste samples**

| Solid/Name  | Waste  | European List of Waste code, origin of waste  |
|-------------|--|---|
| S1          | Air pollution control (APC) residue, bicarbonate process | 19 01 07* (Wastes from incineration or pyrolysis of waste, Solid waste from gas treatment)  |
| S2          | APC residue, lime process                                | 19 01 07* (see above)   |
| S3          | MSWI fly ash   | 19 01 05* (Filter cake from gas treatment)  |
| S4          | APC residue industrial waste #1                          | 19 01 07* (see above)   |
| S5          | APC residue industrial waste #2                          | 19 01 07* (see above)   |
| S6          | Industrial waste bottom ash                              | 19 01 11* (Bottom ash and slag containing dangerous substances)   |
| S7          | Metallic dust from aluminum industry                     | 10 03 19 * (Flue-gas dust containing dangerous substances)  |
| S8-DON      | Packages and materials #1                                | No information  |
| S8-GEO      | Packages and materials #2                                | 19 12 11* (Other wastes (including mixtures) from the mechanical treatment of wastes containing hazardous substances)   |
| S8-SAR      | Packages and materials #3                                | 19 12 11* (see above)   |
| S8-SCO      | Packages and materials #4                                | 15 01 10* (Packaging containing residues of hazardous or contaminated by residues).   |
| S8-TRI      | Packages and materials #5                                | No information  |
| S9-GEO      | Pasty waste #1   | 19 08 13* (Sludges containing dangerous substances from other industrial water treatment plant)   |
| S9-SCO      | Pasty waste #2   | 08 01 13* (Sludges from paint or varnish containing organic solvents or other dangerous substances),<br>08 04 11* (Adhesives and sealants sludges containing organic solvents or other hazardous substances)  |
| S18         | Solid recovered fuel                                     | 19 02 09*Solid fuel waste containing hazardous substances   |
|             |  |   |
| Liquid/Name |  |   |
| S9-SAR      | Pasty waste #3   | Mix of storage tank   |
| S10         | Engine oil   | 13 02 08* (Other motor oils, gear and lubricating)  |
| S11         | Hydraulic oil  | 13 01 13* (Other hydraulic oils)  |
| S12-SON     | Hydrocarbon #1   | 13 07 03* (Wastes of liquid fuels, Other fuels (including mixtures))  |
| S13-SCO     | Hydrocarbon #2   | 13 05 07* (Water mixed with oil from oil / water separators),<br>13 07 03* (see above)  |
| S13-SON     | Hydrocarbon #3   | Mixture of wastes of oils and liquid fuels without motor and lubricating oil and hydraulic oil  |
| S14-PCX     | Halogenated solvent #1                                   | 07 01 03* (Organic halogenated solvents, washing liquids and mother liquors)  |
| S14-SAN     | Halogenated solvent #2                                   | No information  |
| S14-SAR     | Halogenated solvent #3                                   | 14 06 02* (Other solvents and mixtures of halogenated solvents)   |
| S15         | Non-halogenated solvent #1                               | Other solvents, washing liquids and mother liquors from :<br>07 01 04* (Wastes from the manufacture, formulation, distribution and use (MFSU) of basic organic chemicals),<br>07 02 04* (Waste from MFSU of plastics, rubber and synthetic fibers),<br>07 05 04* (Waste from MFSU pharmaceuticals),<br>07 06 04* (Waste from MFSU of fats, soaps, detergents, disinfectants and cosmetics),<br>07 07 04* (Waste from MFSU chemicals from the fine |

|         |                                      |   |
|---------|--------------------------------------|---|
|         |                                      | chemicals and chemical products not elsewhere specified)  |
| S16-CHI | Waste water #1                       | 16 10 01* mixture of (Aqueous liquid wastes destined for off-site treatment, Aqueous liquid wastes containing dangerous substances).  |
| S16-DUC | Waste water #2, mixture of 13 wastes | 08 04 16 (Waste from MFSU of adhesives and sealants (including waterproofing products, Aqueous liquid waste containing adhesives or sealants other than those mentioned in 08 04 15),<br>11 01 06* (Wastes from chemical surface treatment and coating of metals, Acids not elsewhere specified),<br>11 01 11* (11 01, Aqueous rinsing liquids containing dangerous substances),<br>11 01 13* (11 01, Degreasing wastes containing dangerous substances) ,<br>11 01 98* (11 01, Other wastes containing dangerous substances – note : mirror code of 99 code used in France for hazardous waste),<br>12 01 09* (Wastes from shaping and physical and mechanical processing of metals and plastics, Machining emulsions and solutions free of halogens),<br>12 01 99 (12 01, Wastes not otherwise specified),<br>19 07 03 (Landfill leachate other than those mentioned in 19 07 02) |
| S16-GEO | Waste water #3                       | 19 12 04* Waste from mechanic treatment (by example sorting, shredding, compacting, granulating) not specified elsewhere. Plastics and rubber.  |
| S16-HOM | Waste water #4                       | No information  |
| S16-SAR | Waste water #5                       | 16 10 01* mixture of (Aqueous liquid wastes destined for off-site treatment, Aqueous liquid wastes containing dangerous substances).  |
| S16-SCO | Waste water #6                       | Wash water liquids and mother liquors from :<br>07 01 01* (Wastes from the manufacture, formulation, distribution and use (MFSU) of basic organic chemicals),<br>07 02 01* (Waste from MFSU of plastics, rubber and synthetic fibers),<br>07 03 01* (Wastes from the MFSU of organic dyes and pigments (except 06 11)),<br>07 04 01* (Wastes from the MFSU of organic plant protection products (except 02 01 08, 02 01 09), of wood protection agents (except 03 02) and other biocides),<br>07 05 01* (Waste from MFSU pharmaceuticals),<br>07 06 01* (Waste from MFSU of fats, soaps, detergents, disinfectants and cosmetics),<br>07 07 01(Waste from MFSU chemicals from the fine chemicals and chemical products not elsewhere specified)   |
| S17     | Liquid recovered fuel                | 19 02 08* Liquid fuel waste containing dangerous substances.  |

**Table 3 : pH, redox potential and chromium(VI) and (III) concentrations**

| Samples | pH    | pe    | pe + pH | Cr(VI) (%) | Cr(III) (%) |
|---------|-------|-------|---------|------------|-------------|
| Solid   |       |       |         |            |             |
| S7      | 12.98 | -4.97 | 8.01    |            |             |
| S3      | 12.86 | -1.56 | 11.3    | 0.0010     | 0.0289      |
| S4      | 12.77 | -1.45 | 11.32   | 0.0022     | 0.0248      |
| S5      | 12.76 | -1.41 | 11.35   | 0.0021     | 0.0652      |
| S2      | 12.73 | -1.50 | 11.23   | 0.0011     | 0.0156      |
| S1      | 12.05 | -0.99 | 11.06   | 0.0004     | 0.0044      |
| S6      | 10.81 | -0.76 | 13.16   | 0.0004     | 0.1300      |
| S8-TRI  | 8.68  | 0.90  | 9.58    |            |             |
| S8-SAR  | 8.49  | 1.38  | 9.87    |            |             |
| S9-GEO  | 8.01  | 1.43  | 9.44    |            |             |
| S8-GEO  | 7.86  | 1.74  | 9.6     |            |             |
| S18     | 7.73  | 3.10  | 10.83   |            |             |
| S9-SCO  | 7.38  | 2.36  | 9.74    |            |             |
| S8-DON  | 7.29  | 2.18  | 9.47    |            |             |
| S8-SCO  | 6.84  | 1.92  | 8.76    |            |             |
| Liquid  |       |       |         |            |             |
| S14-SAN | 11.13 | -0.35 | 10.78   |            |             |
| S12-SON | 9.71  | 0.45  | 10.16   |            |             |
| S16-DUC | 7.76  | 12.17 | 19.93   |            |             |
| S10     | 7.62  | 0.11  | 7.73    |            |             |
| S16-SAR | 7.43  | -3.51 | 3.92    |            |             |
| S13-SON | 6.75  | 1.30  | 8.05    |            |             |
| S11     | 6.73  | 0.99  | 7.72    |            |             |
| S16-GEO | 6.72  | -1.85 | 4.87    |            |             |
| S16-SCO | 6.65  | 0.10  | 6.75    |            |             |
| S13-SCO | 6.60  | 1.22  | 7.82    |            |             |
| S16-CHI | 6.40  | -1.14 | 5.26    |            |             |
| S14-SAR | 6.00  | 2.98  | 8.98    |            |             |
| S9-SAR  | 5.13  | -0.18 | 4.95    |            |             |
| S17     | 5.11  | 3.30  | 8.41    |            |             |
| S15     | 3.24  | 3.65  | 6.89    |            |             |
| S14-PCX | 2.78  | 6.21  | 8.99    |            |             |
| S16-HOM | 1.50  | 12.17 | 13.67   | 0.2739     | 0.4191      |

**Table 4 : Number and cumulative concentrations of substances with CAS numbers, excluding metal**

| Sample  | Lab1                             |                             | Lab2                             |                             |
|---------|----------------------------------|-----------------------------|----------------------------------|-----------------------------|
|         | N. of substances with CAS number | Cumulated concentration (%) | N. of substances with CAS number | Cumulated concentration (%) |
| Solid   |                                  |                             |                                  |                             |
| S1      |                                  |                             | 1                                | 0.00                        |
| S2      | 1                                | 0.00                        | 1                                | 0.00                        |
| S3      |                                  |                             | 1                                | 0.00                        |
| S4      | 1                                | 0.00                        | 16                               | 0.01                        |
| S5      | 1                                | 0.00                        | 14                               | 0.00                        |
| S6      | 18                               | 0.11                        | 35                               | 0.03                        |
| S7      | 13                               | 0.04                        | 43                               | 0.07                        |
| S8-DON  | 29                               | 0.22                        | 95                               | 0.24                        |
| S8-GEO  | 35                               | 0.16                        | 59                               | 1.50                        |
| S8-SAR  | 23                               | 1.96                        | 82                               | 0.58                        |
| S8-SCO  | 30                               | 0.17                        | 110                              | 0.40                        |
| S8-TRI  | 49                               | 0.17                        | 69                               | 0.20                        |
| S9-GEO  | 26                               | 0.09                        | 86                               | 0.13                        |
| S9-SCO  | 37                               | 1.70                        | 101                              | 4.60                        |
| S18     | 11                               | 2.06                        | 82                               | 2.42                        |
| Liquid  |                                  |                             |                                  |                             |
| S9-SAR  | 36                               | 0.44                        | 106                              | 1.02                        |
| S10     | 20                               | 1.90                        | 51                               | 2.55                        |
| S11     | 11                               | 0.05                        | 30                               | 1.73                        |
| S12-SON | 31                               | 0.30                        | 84                               | 8.23                        |
| S13-SCO | 21                               | 2.87                        | 73                               | 13.78                       |
| S13-SON | 13                               | 0.02                        | 35                               | 0.11                        |
| S14-PCX | 17                               | 56.28                       | 45                               | 27.14                       |
| S14-SAN | 22                               | 8.86                        | 53                               | 0.31                        |
| S14-SAR | 7                                | 62.87                       | 35                               | 81.77                       |
| S15     | 18                               | 43.26                       | 56                               | 23.06                       |
| S16-CHI | 14                               | 0.26                        | 80                               | 0.14                        |
| S16-DUC | 6                                | 0.05                        | 25                               | 0.10                        |
| S16-GEO | 3                                | 0.01                        | 13                               | 0.10                        |
| S16-HOM | 1                                | 0.01                        | 4                                | 0.10                        |
| S16-SAR | 18                               | 0.19                        | 71                               | 0.25                        |
| S16-SCO | 7                                | 0.50                        | 88                               | 0.14                        |
| S17     | 30                               | 11.06                       | 117                              | 15.66                       |

Solid : % w/w dry matter, liquid : % w/w raw matter

**Table 5 : Analytical mass balance of solid samples (NEOC = non extractible organic compounds, VOC = volatile organic compounds, SVOC = semi-volatile organic compounds, TPH = total petroleum hydrocarbons)**

| Concentration (%) | Lab1         |        |       |      |      |       |                        |        | Lab2         |         |       |      |      |                        |        |
|-------------------|--------------|--------|-------|------|------|-------|------------------------|--------|--------------|---------|-------|------|------|------------------------|--------|
| Sample            | Ash – Metals | Metals | NEOC  | VOC  | SVOC | TPH   | Regulate d subs tances | Total  | Ash - Metals | Metal s | NEOC  | VOC  | SVOC | Regulat ed subs tances | Total  |
| S1                | 43.82        | 38.88  | 43.30 | 0.00 | 0.00 |       | 0.00                   | 126.00 | 54.72        | 39.28   | 5.96  | 0.00 | 0.00 | 0.00                   | 99.96  |
| S2                | 39.32        | 56.48  | 2.90  | 0.00 | 0.00 |       | 0.00                   | 98.70  | 63.75        | 36.05   | 0.03  | 0.00 | 0.00 | 0.00                   | 99.83  |
| S3                | 41.13        | 53.77  | 4.50  | 0.00 | 0.00 |       | 0.00                   | 99.40  | 55.24        | 44.16   | 0.19  | 0.00 | 0.00 | 0.00                   | 99.59  |
| S4                | 58.75        | 30.25  | 2.20  | 0.00 | 0.00 | 0.01  | 0.00                   | 91.21  | 66.21        | 33.49   | 0.10  | 0.00 | 0.00 | 0.00                   | 99.81  |
| S5                | 58.66        | 30.34  | 3.30  | 0.00 | 0.00 | 0.01  | 0.00                   | 92.31  | 66.17        | 33.43   | 0.20  | 0.00 | 0.00 | 0.00                   | 99.80  |
| S6                | 46.40        | 40.60  | 9.60  | 0.11 | 0.00 | 0.56  | 0.00                   | 97.26  | 57.97        | 32.53   | 5.30  | 0.03 | 0.00 | 0.00                   | 95.83  |
| S7                | 32.64        | 52.96  | 9.20  | 0.00 | 0.04 | 0.20  |                        | 95.05  | 62.47        | 36.83   | 1.98  | 0.00 | 0.07 | 0.00                   | 101.35 |
| S8-DON            | -7.74        | 28.14  | 40.10 | 0.22 | 0.01 | 4.19  |                        | 64.91  | 4.02         | 8.48    | 67.30 | 0.06 | 0.07 | 0.10                   | 80.04  |
| S8-GEO            | -24.03       | 48.73  | 43.90 | 0.13 | 0.03 | 6.84  |                        | 75.60  | 12.33        | 12.87   | 62.90 | 1.40 | 0.00 | 0.10                   | 89.60  |
| S8-SAR            | 18.55        | 27.45  | 51.00 | 1.35 | 0.00 | 6.24  |                        | 104.59 | 27.52        | 10.58   | 52.60 | 0.06 | 0.47 | 0.10                   | 91.34  |
| S8-SCO            | 2.33         | 5.07   | 74.20 | 0.13 | 0.04 | 2.75  |                        | 84.52  | 19.60        | 3.30    | 77.20 | 0.12 | 0.18 | 0.10                   | 100.50 |
| S8-TRI            | -1.84        | 21.54  | 16.40 | 0.14 | 1.32 | 3.32  |                        | 40.88  | 15.24        | 8.11    | 43.90 | 0.09 | 0.02 | 0.10                   | 67.45  |
| S9-GEO            | 42.59        | 40.11  | 13.50 | 0.01 | 0.09 | 3.74  |                        | 100.03 | 71.50        | 13.50   | 0.11  | 0.03 | 0.11 | 0.00                   | 85.24  |
| S9-SCO            | 25.59        | 43.21  | 19.70 | 1.53 | 0.17 | 10.60 |                        | 100.80 | 37.18        | 19.12   | 18.50 | 2.53 | 2.09 | 0.00                   | 79.41  |
| S18               | -8.27        | 26.37  | 69.60 | 1.91 | 0.15 | 8.85  |                        | 98.61  | 22.69        | 7.61    | 61.50 | 0.01 | 2.47 | 0.11                   | 94.39  |

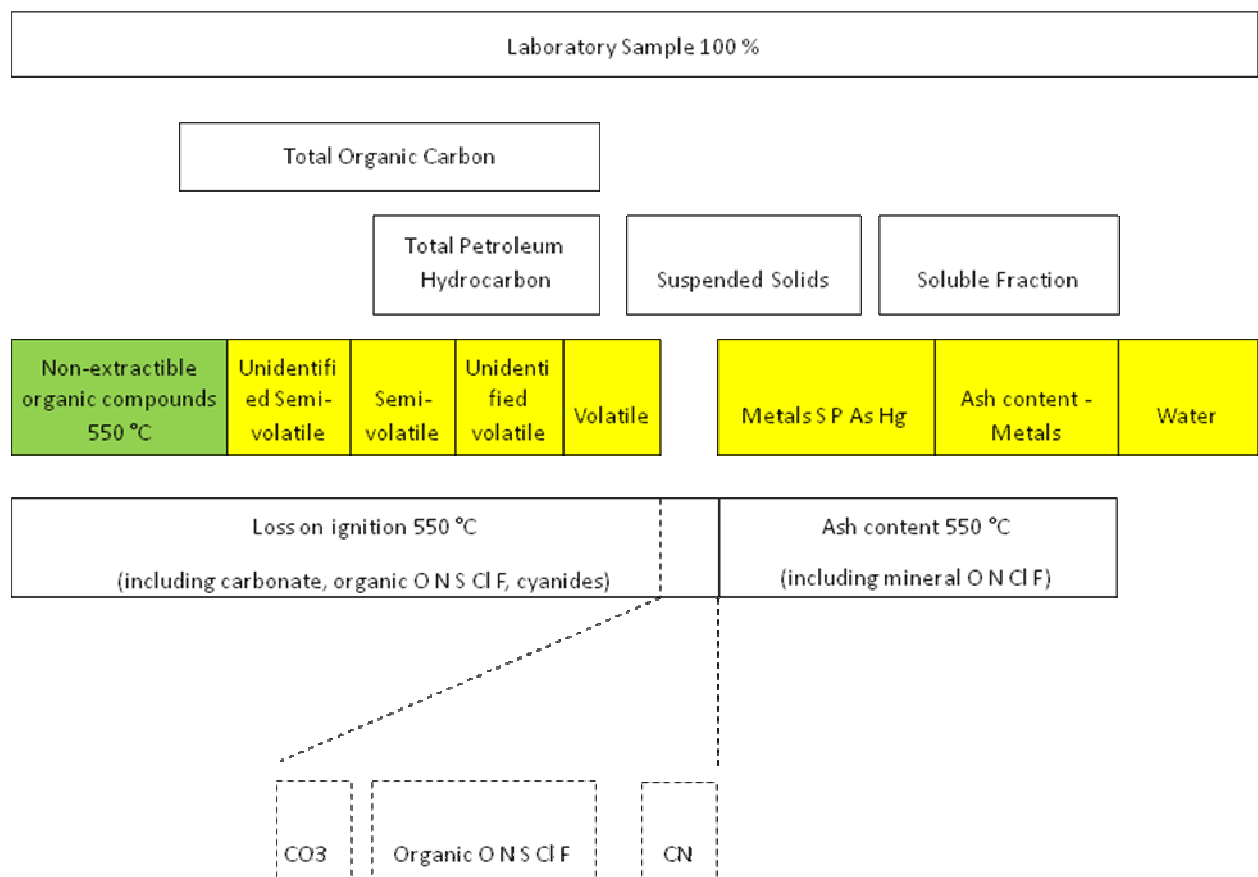
**Table 6 : Analytical mass balance of liquids (SVOC = semi-volatile organic compounds, VOC = volatile organic compounds, vTPH = volatile total petroleum hydrocarbons, TPH = total petroleum hydrocarbons, USVOC = unidentified SVOC, UVOC = unidentified VOC)**

| Concentration (%) | Lab1   |              |        |      |       |      |       |                      |        | Lab2  |              |        |       |       |      |       |                      |        |
|-------------------|--------|--------------|--------|------|-------|------|-------|----------------------|--------|-------|--------------|--------|-------|-------|------|-------|----------------------|--------|
| Sample            | Water  | Ash – Metals | Metals | SVOC | VOC   | vTPH | TPH   | Regulated substances | Total  | Water | Ash - Metals | Metals | USVOC | SVOC  | UVOC | VOC   | Regulated substances | Total  |
| S9-SAR            | 97.77  | -3.50        | 4.80   | 0.00 | 0.43  | 0.02 | 5.23  | 0.02                 | 104.76 | 74.74 | 10.36        | 3.54   | 6.67  | 0.65  | 0.00 | 0.10  | 0.10                 | 96.16  |
| S10               | 5.01   | 0.49         | 0.21   | 0.00 | 1.90  | 0.00 | 80.20 |                      | 87.80  | 5.00  | 0.08         | 0.72   | 0.00  | 1.69  | 0.63 | 0.76  | 0.11                 | 84.72  |
| S11               | 1.76   | -0.10        | 0.10   | 0.00 | 0.04  | 0.05 | 85.50 | 0.01                 | 87.36  | 1.40  | -0.31        | 0.31   | 79.40 | 1.54  | 0.30 | 0.09  | 0.11                 | 82.83  |
| S12-SON           | 0.46   | 0.11         | 0.09   | 0.19 | 0.08  | 0.05 | 22.00 | 0.03                 | 23.01  | 0.20  | -0.81        | 0.81   | 61.48 | 7.23  | 0.48 | 0.00  | 1.01                 | 70.39  |
| S13-SCO           | 59.16  | 1.19         | 2.61   | 0.00 | 2.68  | 1.56 | 28.40 | 0.19                 | 95.79  | 57.60 | 3.30         | 1.90   | 34.97 | 13.18 | 1.02 | 0.42  | 0.36                 | 112.74 |
| S13-SON           | 97.24  | -0.15        | 0.15   | 0.00 | 0.01  | 0.00 | 0.01  | 0.01                 | 97.27  | 97.00 | -0.01        | 0.11   | 0.04  | 0.01  |      | 0.00  | 0.11                 | 97.25  |
| S14-PCX           | 0.01   | -0.03        | 0.03   | 0.21 | 56.06 | 0.37 | 5.51  | 0.01                 | 62.17  | 0.10  | -0.04        | 0.04   |       | 0.14  |      | 26.91 | 0.10                 | 27.25  |
| S14-SAN           | 81.26  | 3.42         | 2.95   | 0.00 | 8.46  | 0.01 | 0.13  | 0.35                 | 96.58  | 76.55 | 2.39         | 4.38   | 0.01  | 0.00  | 0.00 | 0.15  | 0.15                 | 83.63  |
| S14-SAR           | 6.10   | 2.27         | 0.23   | 0.01 | 62.84 | 0.13 | 0.38  | 0.02                 | 71.97  | 6.70  | -0.06        | 0.26   | 0.49  | 0.23  |      | 81.44 | 0.10                 | 89.16  |
| S15               | 10.52  | -0.35        | 0.65   | 0.57 | 39.38 | 6.70 | 5.67  | 3.30                 | 66.45  | 10.10 | -0.16        | 0.36   | 15.04 | 4.19  | 9.44 | 13.64 | 5.28                 | 57.88  |
| S16-CHI           | 99.17  | 0.00         | 1.80   | 0.00 | 0.21  | 0.01 | 0.23  | 0.04                 | 101.47 | 93.00 | 1.45         | 1.25   | 0.03  | 0.01  | 0.04 | 0.03  | 0.10                 | 95.92  |
| S16-DUC           | 98.76  | -0.51        | 0.81   | 0.00 | 0.04  | 0.00 | 0.07  | 0.01                 | 99.18  | 96.00 | 0.35         | 0.35   | 0.03  | 0.00  | 0.00 | 0.00  | 0.10                 | 96.83  |
| S16-GEO           | 100.00 | 0.01         | 0.09   | 0.00 | 0.00  | 0.00 |       | 0.01                 | 100.11 | 97.00 | 0.03         | 0.07   | 0.00  | 0.00  | 0.00 | 0.00  | 0.10                 | 97.20  |
| S16-HOM           | 94.30  | 0.96         | 4.14   | 0.00 | 0.00  | 0.00 |       | 0.01                 | 99.41  | 96.00 | 1.36         | 3.94   |       | 0.00  |      | 0.00  | 0.10                 | 101.40 |
| S16-SAR           | 88.15  | -0.26        | 0.26   | 0.00 | 0.01  | 0.00 | 0.08  | 0.18                 | 88.42  | 97.00 | 0.05         | 0.15   | 0.15  | 0.04  |      | 0.00  | 0.21                 | 97.60  |
| S16-SCO           | 87.79  | 4.03         | 1.37   | 0.00 | 0.42  | 0.12 | 3.89  | 0.09                 | 97.70  | 89.00 | 0.75         | 0.75   | 0.01  | 0.00  | 0.04 | 0.04  | 0.10                 | 90.69  |
| S17               | 11.59  | -3.39        | 3.49   | 0.00 | 10.95 | 4.67 | 19.6  | 0.10                 | 47.00  | 11.09 | 4.00         | 0.00   | 39.79 | 10.21 | 0.00 | 0.98  | 0.10                 | 66.18  |



|    |  |
|----|--|
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| 4  | Figure 1 : Conceptual scheme of wastes composition (dashed line: not measured in the protocol)             |
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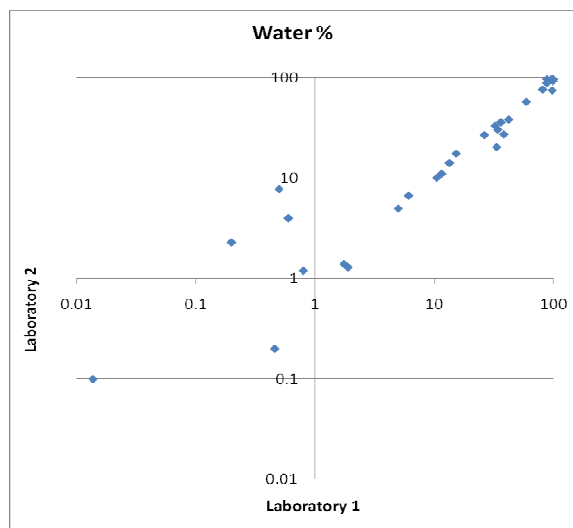
4 Figure 1

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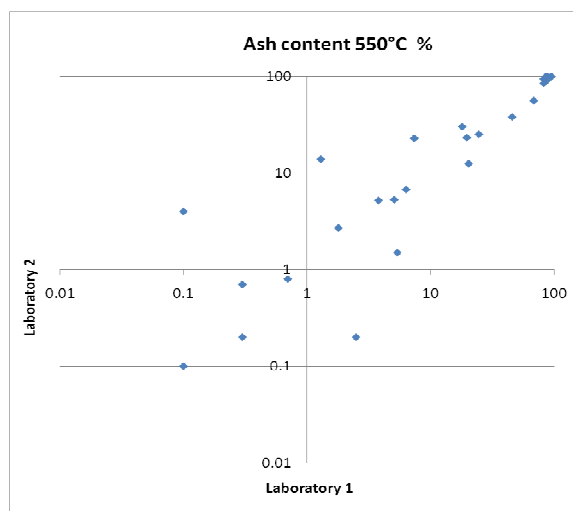
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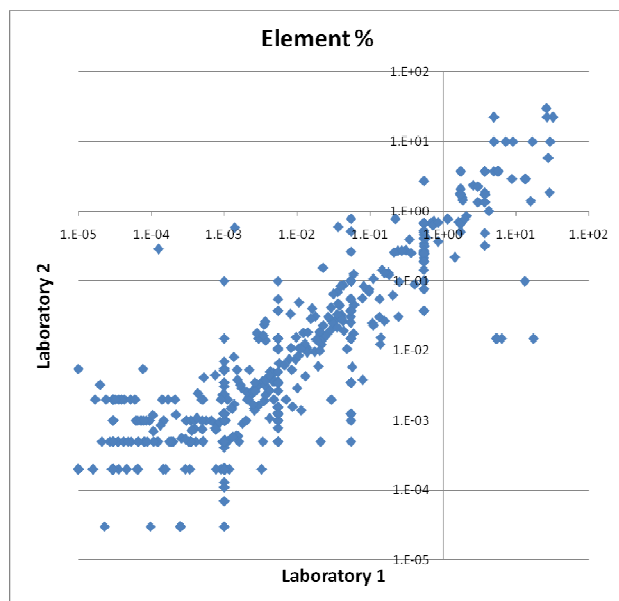
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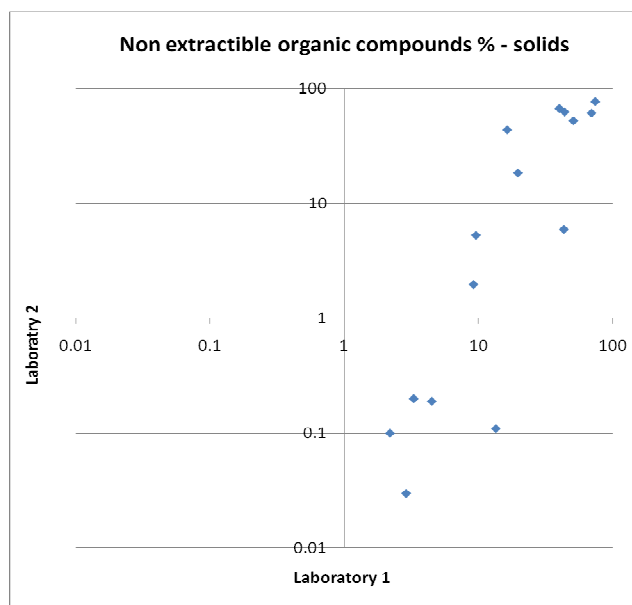
**Figure 2**



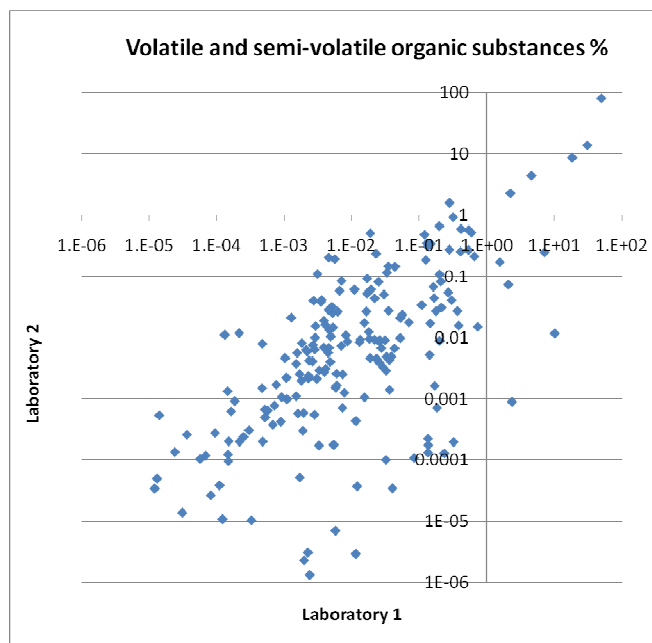
**Figure 3**



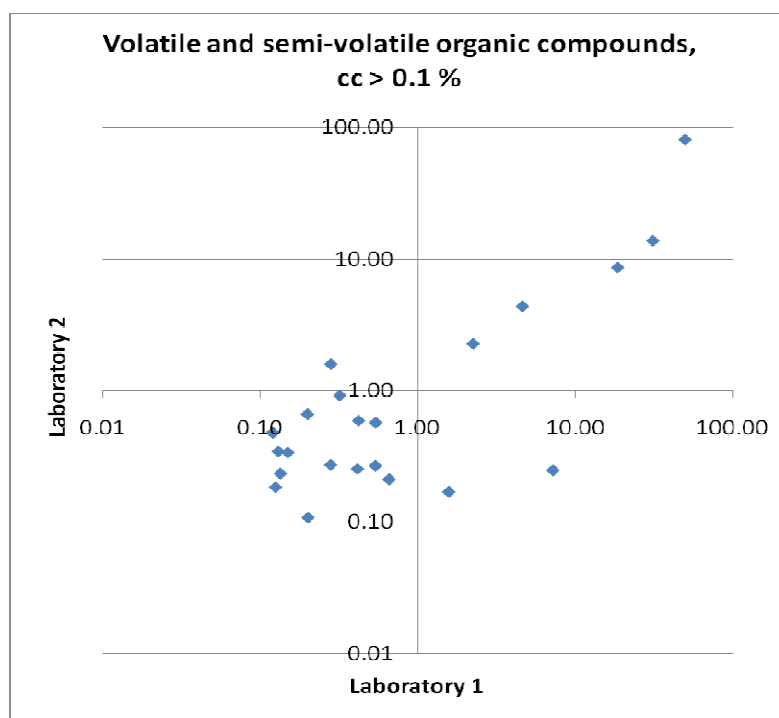
**Figure 4**



**Figure 5**



**Figure 6**



**Figure 7**